



Response to "comment on 'Trends in the exchange current for hydrogen evolution' [J. Electrochem. Soc., 152, J23 (2005)]"

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Response to “Comment on ‘Trends in the Exchange Current for Hydrogen Evolution’ [*J. Electrochem. Soc.*, **152**, J23 (2005)]”

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As pointed out by Schmickler and Trasatti¹ and in our paper,² the concept of volcano plots of the rate of the hydrogen evolution reaction (HER) as a function of the hydrogen binding energy to the metal surface was pioneered several decades ago. Our small, new contribution is a way of obtaining the hydrogen adsorption energy using density functional theory calculations. The main advantage of this approach is that it can be used quite simply to make predictions for new systems. This has already been shown by Kibler and Kolb³ to be useful in understanding the trends in the HER on Pd overlayers on a range of systems. The same approach has also been able to rationalize why active sites in the hydrogenase and nitrogenase enzymes are good for hydrogen evolution and to predict that MoS₂ nanoparticles should be reasonable HER catalysts.⁴

The calculated databases of hydrogen adsorption energies also provide a simple and straightforward way of studying trends. They do not support the notion that the metal–H bond on Au should be as strong as that to, e.g., Ni. This is a significant difference which reflects the large difference in the electronic structure of Au and Ni. Au has filled d bands and Ni has partly empty d bands, leading to partly empty antibonding H–Ni states.⁵ It is difficult to see how H–H interactions could shift the free energy of H on Ni to significantly above the chemical potential of the reactants and products in the HER.

In our paper we introduce a simple kinetic model to show how a volcano with a maximum close to $G_{\text{H}} = 0$ can be obtained. As

pointed out in the paper, “we concentrate on the trends in exchange rates from one metal to the next and on the contribution to these trends originating directly from the variations in the thermochemistry....” More sophisticated models have been introduced showing the same trend, and we should have referenced the pioneering work of Parsons⁶ in this connection. Our model leaves ample room for improvement, in particular when we have new molecular level insight into the processes. The basic notion that $G_{\text{H}} = 0$ is a necessary (but not sufficient) condition for a good catalyst should be generally valid.⁶ We note that for our simple, completely symmetrical model it is actually correct that at equilibrium all rates are the same.

In summary, our approach provides a new method for obtaining H adsorption free energies for electrochemically interesting systems. It concentrates on understanding trends and it has already proven to have predictive power.

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